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Chemical activation of calcium aluminate cement composites cured at elevated temperature

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ABSTRACT

The influence of sodium sulfate, as an activator, on the hydration of calcium aluminate cement (CAC)–fly ash (FA)–silica fume (SF) composites was investigated. Different mixes of CAC with 20% pozzolans (20% FA, 20% SF and 10% FA + 10% SF) were prepared and hydrated at 38 °C for up to 28 days. The hydration products were investigated by XRD, DSC and SEM. The results showed that sodium sulfate accelerated the hydration reactions of calcium aluminate cement as well as the reactions of FA and SF with CAH_{10} and C_2AH_8 to form the strätlingite (C_2ASH_8). The later reactions prevent the strength loss by preventing the conversion of CAH_{10} and C_2AH_8 to the cubic C_3AH_6 phase. The acceleration effect of Na_2SO_4 on the reactivity of fly ash was more pronounced than on the reactivity of silica fume with respect to reaction with CAH_{10} and C_2AH_8 phases.

1. Introduction

Calcium aluminate cement (CAC) has many industrial applications due to its advanced properties, such as rapid strength development, high temperature resistance and resistance to a wide range of chemically aggressive conditions. It is used in refractories, pipes, sewer constructions, industrial floors and dam spillways [1,2].

High early strength is one of the major advantages of calcium aluminate cement over Portland cement (PC). However, the high early strength may mislead designers to ignore the conversion reaction of calcium aluminate cement which causes strength loss in hot and humid conditions. The hydration products of CAC depend on the curing temperature [1–5]. CAH_{10} is the main hydration products at temperatures less than 20 °C. However, C_2AH_8 and AH_3 are the main hydration products above 20 °C. The high early strength of CAC cement is attributed to the formation of hexagonal hydrates (CAH_{10} and C_2AH_8) as the dominant hydration products [3]. However, CAH_{10} and C_2AH_8 are known to be metastable and convert to the more stable C_3AH_6 and AH_3 [3,6,7], according to the following equations [3]:

$$3CAH_{10} \rightarrow C_3AH_6 + 2AH_3 + 18H^* \quad (1)$$

$$3C_2AH_8 \rightarrow 2C_3AH_6 + AH_3 + 9H \quad (2)$$

The conversion reactions are accelerated at high temperatures and moisture contents [8]. The conversion reactions are associated with the strength loss and the formation of microcracks in the concrete structure [8–10].

Midgley [11] stated that traces strätlingite (C_2ASH_8) were detected in aged hydrated high alumina cement. Midgley [11] suggested that strätlingite compound has better mechanical properties than hydrogarnet (C_3AH_6). Bentsen et al. [12] reported that microsilica enhances the formation of strätlingite. He also stated that the strätlingite compound crystallizes as a stable phase in the temperature range of 20–70 °C.

Mixing pozzolan with CAC was found to prevent the conversion reaction [13–18]. Majumdar and Singh [13] found that slag addition to CAC prevented the strength loss for the pastes cured under water at 40 °C. The ability of slag to prevent the conversion reactions was correlated with its hydraulic activity [19,20], which depended on the glass contents and the dissolution ability in basic solutions. Silica fume and fly ash are high reactive pozzolans [21]. Silica fume reacts in few minutes and gave large amount of silicate ions [21] in solution. ASTM C 373-88 [23] found the presence of sodium ions accelerates dissolution of silica required for stratlingite formation.

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In the present work, the possibility of using two types of pozzolanic materials (SF & FA) with calcium aluminate cement (CAC) to prepare blended cements mixes suitable for hot climate was investigated. The effect of sodium sulfate as an activator on the hydration characteristics of these blends was also investigated at elevated temperature.

2. Materials and methods

2.1. Materials

Silica fume (SF) was obtained from Ferrosilicon Co. Edfo, Egypt. Fly ash (FA) was supplied by ASH RESOURCES (PTY) LTD (Dura Pozz), India. Calcium aluminate cement (CAC) was obtained from Suez Cement Company, Suez, Egypt. The chemical compositions of the raw materials are given in Table 1.

2.2. Preparation of cement pastes

Each of the two types of pozzolans was replaced 20% of CAC to produce blended cements. In addition 10% of each pozzolan was used together to replace CAC. These mixes were designated as shown in Table 2. The water of normal consistency was determined in accordance with B.S. 4550. The water required for standard consistency is presented in Table 2. The required amount of water (with and without Na_2SO_4) was mechanically mixed with the cement blends for 3 min. The pastes were then poured and compacted into 1-in. cube moulds and their surfaces were smoothened. The moulds were placed in a humidity cabinet having about 100% RH at 23 ± 2 °C for 24 h. After demoulding, the cubes were placed under water at 38 °C until testing (1, 3, 7 and 28 days).

2.3. Methods of investigation

The compressive strength measurements were conducted on three samples of each paste at a given curing period. Apparent porosity was determined using the standard liquid volume method adopted by the ASTM C 373-88 [23]. X-ray diffraction (XRD) analysis was performed using an automated diffractometer (Philips type: PW1840), at a step size of 0.02°, scanning rate of 2° in 2θ/min., and a 2θ range from 4° to 80°. Differential scanning calorimetry runs were conducted using a Shimadzu DSC-50 thermal analyzer at a heating rate of 10 °C/min. The fracture surfaces hydrated pastes were investigated by using SEM (JOEL, Model: JSM-5600, Japan.) equipped with secondary electron detector and EDX. All samples were coated with gold.

Table 1
Chemical compositions of CAC, FA and SF (mass%).

Oxides	CAC	FA	SF
SiO_2	5.39	62.26	95.57
Al_2O_3	48.75	26.89	0.30
Fe_2O_3	1.44	4.19	1.35
CaO	39.12	0.76	0.19
MgO	0.21	0.53	0.34
SO_3	0.15	0.31	0.11
K_2O	0.10	1.12	0.51
Na_2O	0.14	0.07	0.19
Cl	–	0.04	–
TiO_2	2.52	1.77	0.02
MnO_2	0.17	0.09	–
P_2O_5	–	0.37	0.03
L.O.I	0.53	1.42	1.10
Surface area (cm^2/g)	3650	3850	≈20,000

Table 2
Mix compositions of investigated specimens.

Mix	Compositions (mass%)			
	CAC	FA	SF	W/C[a]
Mo	100	–	–	0.25
Ma	80	20	–	0.28
Mb	80	10	10	0.295
Mc	80	–	20	0.31

[a] Water/cement ratio required for standard consistency.

3. Results and discussion

3.1. Physico-mechanical properties

3.1.1. Apparent porosity

Fig. 1, represents the apparent porosities of the hydrated pastes cured for 28 days at 38 °C for both the neat calcium aluminate cement (shown as separate point in the graph) and the blended mixes with different amounts of Na_2SO_4. The porosities of mixes Ma, Mb and Mc are lower than this of the neat calcium aluminate cement (Mo). Due to the relatively higher surface area of the silica fume more than the fly ash, mixes which contain silica fume (Mb and Mc) show lower porosities than those which contain only fly ash (Ma). The same increase of porosity was observed in Portland cement-SF system [24]. It is found that addition of Na_2SO_4 has a remarkable effect on the porosity. The porosity decreases with increasing Na_2SO_4 contents for each mix.

3.1.2. Compressive strength

Figs. 2 and 3 represent the results of compressive strength as a function of curing times of mixes (Mo, Ma, Mb and Mc) prepared with 2% and 3.5% wt. Na_2SO_4 respectively. The compressive strength of the neat CAC paste (Mo) increased with time up to 3 days then decreased up to 28 days. The high early compressive strength is a characteristic property of CAC cements, especially at low W/C ratio and high temperature [8,25]. The compressive strength of blended CAC mixes (Ma, Mb and Mc) with 2% and 3.5% Na_2SO_4 showed continues increase with curing time. In general, the strength values of pastes containing 3.5% Na_2SO_4 are higher than those containing 2% Na_2SO_4.

Fig. 4 represents the compressive strength of pastes hydrated for 28 days. It clearly shows the difference between the

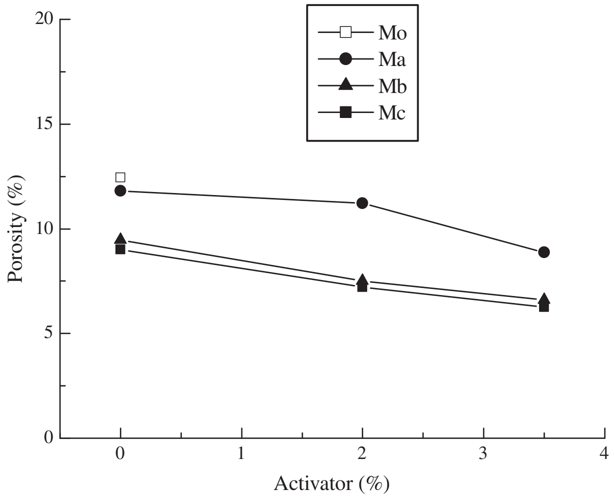

Fig. 1. Apparent porosity of hardened pastes with different amount of activator cured at 38 °C for 28 days (sample Mo without activator).